

Received April 30, 2012; reviewed; accepted February 27, 2013

REMOVAL OF METHYLENE BLUE BY NATURAL AND Ca AND K-EXCHANGED ZEOLITE TREATED WITH HYDROGEN PEROXIDE

Murat CANLI*, Yuksel ABALI*, Salih Ugur BAYCA**

* Faculty of Arts and Sciences, Celal Bayar University, 45140, Manisa, Turkey; murcanli@yahoo.com; yabali@yahoo.com

** Soma Vocational School, Celal Bayar University, Soma/Manisa, Turkey; salihbayca@gmail.com

Abstract: A comparison was made of influence of physically adsorbed methylene blue (MB) dye on the physicochemical properties of Manisa-Akdere zeolite (natural zeolite) and zeolite modified with K and Ca (all samples treated with hydrogen peroxide before modification) using batch adsorption technique. After elementary characterization of this adsorbent, the effects were investigated of initial MB concentration, pH, contact time, stirring rate, adsorbent dosage and temperature on the selectivity and sensitivity of the removal process. A larger adsorption of the dye was observed for modified zeolite (42.7 mg/g) than for natural zeolite (28.6 mg/g) per gram of an adsorbent after all zeolite samples treated with hydrogen peroxide. Zeolite treated with H₂O₂ showed higher adsorption capacity than untreated zeolite samples. The Langmuir model (R^2 values between 0.959 and 0.996) fitted the experimental data better than the Freundlich model (R^2 values between 0.804 and 0.988). The adsorption process was found to be slightly influenced by adsorbent dosage, contact time and temperature. Optimum pH for adsorption of MB was found to be at 7. Adsorption equilibrium attained within 30 minutes. The sorption of MB increased slightly with rising temperature. In addition, adsorption values rose with modification Ca-Exchanged (after H₂O₂ treatment) > K-Exchanged (after H₂O₂ treatment) > Zeolite treated with H₂O₂ > Ca-Exchanged > K-Exchanged > Natural Zeolite.

Keywords: dye adsorption, methylene blue, adsorption, isotherms, zeolite, alumino-silicate, hydrogen peroxide

Introduction

Growth in population, oil consumption, exhaust emissions, industrial activities, energy production, and frequently uncontrolled pesticide use resulted in the accumulation of hazardous inorganic and organic pollutants in the environment (Misaelidis, 2011). Moreover, if the concentration of pollutants exceeds certain limits, their presence causes danger to the environment and to human health. In order to minimize such

danger, various precautions should be taken such as waste stabilization and environmental remediation. This can largely be accomplished by extraction of the pollutants from soils or aqueous systems and reduction of their mobility.

The textile and printing industries produce and dump highly colored waste effluents from the use of dyes and pigments, and these wastes cause serious environmental problems. The estimated annual production of more than 10,000 different manufactured dyes is around $7 \cdot 10^8$ kg. These complicated compounds with a high molecular weight resist to biological degradation (Alkan et al., 2007). Even though dyes can be removed from wastewaters by coagulation, flocculation, biodegradation and oxidation, these methods are expensive and often ineffective (Armagan et al., 2003; Metes et al., 2004).

Therefore, recent studies have been focused on the application of natural mineral clays as low-cost adsorbents to remove colored pollutants (Crini, 2006; Doğan et al., 2009; Fungaroa et al., 2010; Glaysz-Plaska et al. 2000; Gulgonul, 2012; Korkuna et al., 2006; Wang and Peng, 2010). Previous research has shown that several alternative adsorbents have been suggested for MB adsorption like activated carbon or clay minerals, especially, natural and modified zeolites. These aluminosilicates are cheap adsorbents which are widely applied in industry, environment protection, agriculture, medicine, and many other fields (Gümüş and Akbal, 2011; Farhade and Aziz, 2010). The molecular-sieve properties, availability of strongly active surface sites, high resistance to acids and other useful properties of zeolites allow the use of them as catalysts in cracking, hydrocracking, isomerization and other processes (Alzaydien, 2009; Jin et al., 2008). There are several rich reserves of zeolite in Turkey (Albayrak, 2008).

The application of natural zeolites to the environmental remediation is mainly based on their ion-exchange properties (Doğan et al., 2000). It is well-known that ion-exchange in the case of zeolites takes place among cations and they must be modified to provide them with anion sorption properties. Aluminosilicate catalysts are characterized according to their activity, selectivity, stability and their capability of multiple regeneration (Ozdemir, 2008). Natural and modified zeolite are natural minerals composed of the aluminosilicate matrix with a variety of other metal oxides and metal cations embedded (Hernandez et al., 2000; Doğan et al., 2008; Caglar et al., 2009). Zeolite with three 8-membered rings and one 10-membered ring has net negative surface charge which is counterbalanced by monovalent (Na^+ , K^+) and divalent (Ca^{2+}) cations. Zeolites can be ion exchanged using metal ions like Fe, Cu, Mn, Ca, and Ba. Zeolites are negatively charged because of the substitution of Si (IV) by Al (III) in the tetrahedral accounts for a negative charge of the structure. The Si/Al ratio determines the properties of zeolites such as ion exchange capacity.

Before applying zeolitic tuff (natural zeolite) to adsorption process, several activation methods are suggested in previous studies for increasing the adsorption capacity of zeolite such as acid activation (Ajemba and Onukwuli, 2013; Kowalczyk et al., 2006), heat activation (Ates et al., 2011), and modification. Even though heat

activation is an effective way to increase the surface area and capacity on an adsorbent, the use of acid activation results in greater increase in surface area and adsorption capacity. Hydrogen peroxide is used for activation of zeolite because of its role as a weak acid. In acidic environments, the oxidation rate of hydrogen peroxide is slow, but faster than basic environments. Modification by metals with mono or bivalent ion also is a way for increasing adsorption capacity of zeolite (Farhade and Aziz, 2010).

The uptake of metal cations from solutions by the zeolites is affected by a variety of factors such as the temperature, the solution pH, the presence of competing cations and complexing agents, the dimensions of the hydrated dissolved species compared to the opening of their channels and the external surface activity (Gurses et al., 2006).

The aim of this article is to show how hydrogen peroxide influences natural and modified zeolite (peroxide applied before modification) in the adsorption of methylene blue. The difference this article from others is that even though H_2O_2 is used in the literature for degradation of MB (Kondru et al., 2009; Slokar and Marechal, 1998; Etaiw and El-Bendary, 2012) and there are several materials already used for activation of zeolite (Ates and Hardacre, 2012; Jia et al., 2009; Hernandez-Ramirez and Holmez, 2008), H_2O_2 was not tried before in activation process of zeolite.

Experimental design

Materials

Natural zeolite samples were obtained from the Demirci-Akdere region, Manisa, Turkey with the general formula of $(K_{2.3} Na_{0.5} Ca_{2.1} Mg_{0.6} Fe(III)_{0.9} Fe(II)_{0.2} Ti_{0.2}) (Si_{31.4} Al_{6.5} O_{44}) 21.8H_2O$ has the chemical composition (in %): SiO_2 , 67.29; TiO_2 , 0.26; Al_2O_3 , 12.32; Fe_2O_3 , 1.26; FeO , 0.25; MgO , 0.29; CaO , 3.01; Na_2O , 0.66; K_2O , 2.76; H_2O , 10.90 (see Table 1), whereby the content of the main mineral was $85 \pm 6\%$. Methylene Blue, MB (Merck, C.I. = 52015, $C_{16}H_{18}N_3SCl$, FW = 373,86 g/mol] was used as a cationic dye adsorbate (see Fig 1).

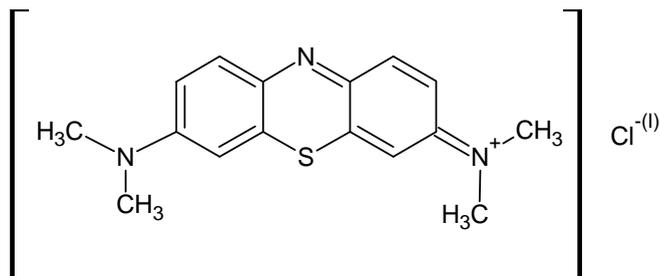


Fig. 1. Chemical structure of methylene blue

Table 1. Physicochemical properties of natural zeolite

Chemical compound	Natural zeolite, %	Zeolite treated with H ₂ O ₂	K-exchanged zeolite	Ca-exchanged zeolite
SiO ₂	73.90	74.87	71.46	70.69
Al ₂ O ₃	14.17	16.12	13.28	12.88
Fe ₂ O ₃	1.451	1.116	1.003	1.113
CaO	2.987	2.637	2.514	5.041
MgO	2.465	2.263	2.221	2.201
K ₂ O	2.939	2.667	6.817	2.438
Na ₂ O	<0.020	<0.043	0.047	<0.030
CEC	106meq/100g	–	–	–
Particle size	<100 μm	–	–	–
Molecular channel size	7.9 Å × 3.5 Å	–	–	–
S _{BET}	37.95m ² /g	40.34 m ² /g	49.06 m ² /g	54.57 m ² /g
Pore volume	0.11cm ³ /g	0.11cm ³ /g	0.11cm ³ /g	0.11cm ³ /g
pH	7.9	7.6	8.7	7.8

Activation and modification of zeolite

Zeolites were transformed into calcium and potassium form after peroxide activation. Before peroxide activation, zeolite was dried in a pre-heated oven at 200 °C for 3 h to get rid of moisture and other impurities. Acid activation was made by H₂O₂ instead of HCl. 5 g of native solids (particle fraction 100 μm) were applied to 250 ml H₂O₂ (50%, hydrogen peroxide) for 24 h at 25 °C. Mixture was centrifuged and dried in oven at 110 °C. On preparation of Ca-exchanged zeolite and K-exchanged zeolite form of zeolite, 50 ml of each solution 1 M CaCl₂ and 1 M KCl mixed with 2 g of zeolite in separate flasks, and then stirred for 24 h. The samples were centrifuged, filtered, washed 10 times with water, dried in oven and ground.

Characterization methods

The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the pore volume (V_p) was determined from low-temperature nitrogen adsorption measured using a Micrometrics Gemini VII analyzer. In determination of the surface area, the samples were degassed at 300 °C before the measurements were taken. The specific surface area was obtained by five points at p/p^0 between 0.1 and 0.99 applying the Brunauer-Emmett-Teller equation to the adsorption data. The phases of the zeolite were determined by X-ray diffraction analyses (XRD) with an automated Philips X'Pert Pro diffractometer with Cu anode using Co K α radiation at 40 kV and 20 mA over the range (2 θ) of 5–80° with a scan time of 1°/min. The chemical composition of zeolite was determined by a Philips X'Pert Pro X-ray fluorescence spectrometer (XRF) equipped with a Rh X-ray tube (operated at 50 kV–60 mA). Scanning Electron micrographs were obtained by using Philips XL-30S FEG scanning

electron microscope (SEM). Thermal analyses were performed by the thermogravimetric analysis (TGA) method (Perkin Elmer Diomand TG/DTA). The types of functionalities of the materials and adsorbed species were determined on the basis of the infrared spectroscopy. The Fourier transform infrared (FT-IR) spectra of natural and modified zeolites (Fig. 3) were recorded in the transmission mode at room temperature on 1725X Perkin-Elmer instrument using KBr pellet technique (1:20) with the resolution 2 cm^{-1} .

Sorption methods

The adsorption was performed by batch experiments. Kinetic experiments were carried out by stirring 100 mL of dye solution of known initial dye concentration (100mg/L) with 0.05 g of zeolite at room temperature ($25\text{ }^{\circ}\text{C}$) at 150 rpm in different 250 ml flasks. After time intervals were completed, solutions were centrifuged at 3500 rpm for 10 min. The concentration in the supernatant solution was analyzed using a UV spectrophotometer (Shimadzu UV-1800) by measuring absorbance at $\lambda_{\text{max}} = 664.4\text{ nm}$ and $\text{pH} = 7$.

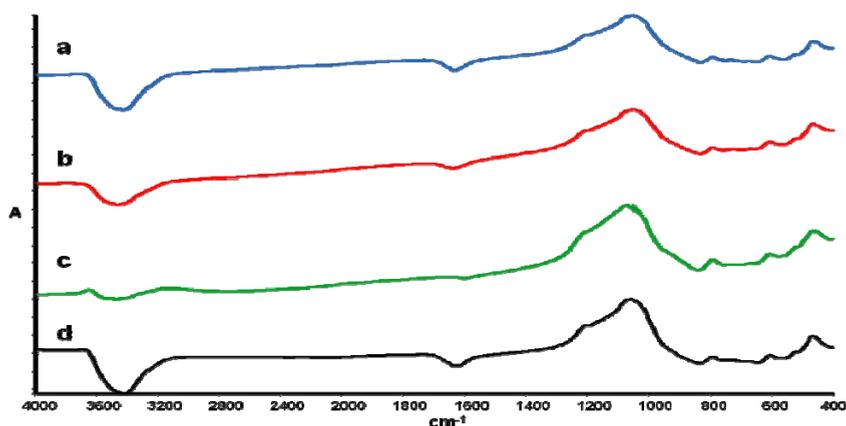


Figure 3. FTIR spectra of ; (a) H_2O_2 treated zeolite, (b) Ca-exchanged zeolite, (c) K- exchanged zeolite and (d) untreated natural zeolite samples

Results and discussion

Surface areas of zeolite samples are found to be $49.06\text{ m}^2/\text{g}$ for K-exc zeolite, $54.57\text{ m}^2/\text{g}$ for Ca-exc zeo, and $37.95\text{ m}^2/\text{g}$ for untreated zeolite. Besides, activating zeolite with H_2O_2 before modification with K and Ca ions caused the increase in BET surface area. After hydrogen peroxide treatment, the surface area of zeolite has become $44.49\text{ m}^2/\text{g}$. It indicates that the metal chlorides switch with exchangeable ions in zeolite like Ca, Mg and K influenced the surface area in positive way. Bivalent ions like Ca increased the surface area more than monovalent ions like K (Han et al., 2009).

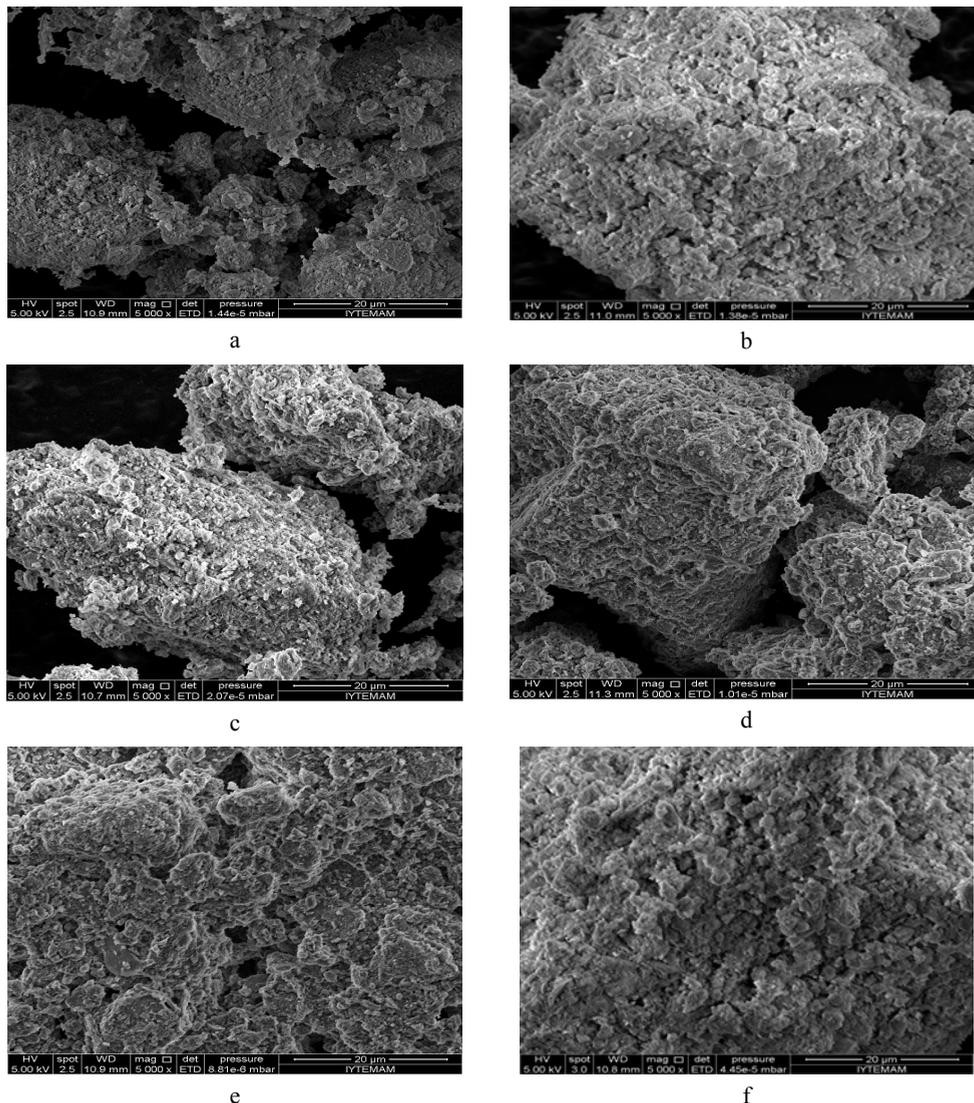


Figure 4. SEM pictures of zeolite samples (a) natural zeolite, (b) zeolite treated with H_2O_2 , (c) K-exchanged zeolite, (d) Ca-exchanged zeolite, (e) Ca-exchanged zeolite after MB adsorption, and (f) K-exchanged zeolite after MB adsorption

FTIR results presented in Fig. 3 shows that modifying zeolite with Ca and K made change in zeolite structure especially in 3400 and 1680 cm^{-1} bands. Chavez et al. (2010) had similar results for Ba adsorption on Ca exchanged zeolite samples. The change in the structure of zeolite samples could be more clearly seen in SEM pictures (see Fig. 4). Activating zeolite with hydrogen peroxide had let more Ca and K ions enter into zeolite surface. The spaces in zeolite structure had been filled with MB by application of modified zeolite on adsorption of MB (see Fig. 4.).

X-ray diffraction patterns of the zeolite samples in (Fig. 5) show that modification of zeolite with solutions did not lead to significant structural changes. The effect of hydrogen peroxide on zeolite appears at decreasing number of peaks because of exchange ions with hydrogen of peroxide. The quantitative XRD analysis demonstrated that the Akdere natural zeolitic tuff consisted of clinoptilolite with minor quantities of quartz, Na-Ca feldspar, mica and opal-CT (Demirhan, 1998). Natural zeolite hardly contains amorphous material. Although, natural zeolite involves both amorphous material which can be seen by means of hump and that of height between 2θ is equal to 208 and 308 (Cu Ka) at XRD diagram and opal-CT that is observed by a flat line with the d-spacing of between 4.05 Å and 4.10 Å (cristobalite-tridimite transition). The X-ray diffraction diagrams of the clinoptilolite samples given in Figure 5 show characteristic clinoptilolite peaks at 2θ (Cu Ka) = 9.878, 22.48 and 308. As Chavez et al. (2010) stated in their study, XRD results also show the increase in peaks below 10° which were caused by Ca and K modification (see Figure 5).

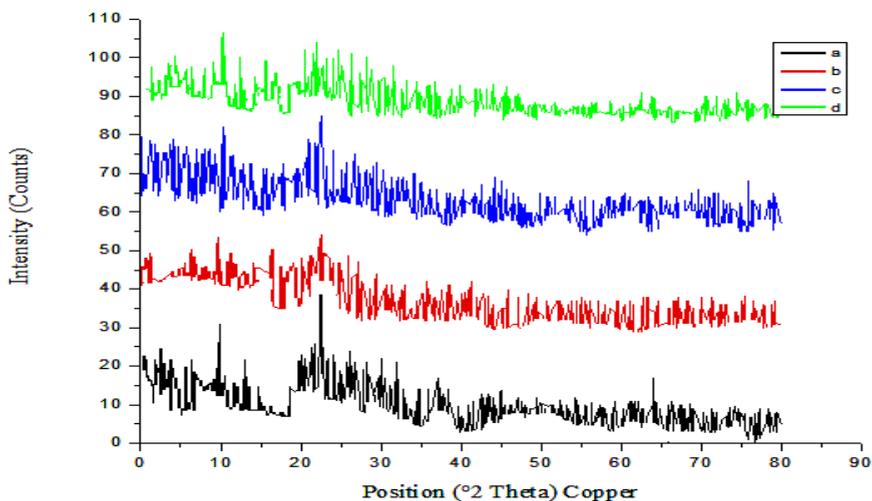


Figure 5. XRD graph of zeolite; a) natural zeolite, b) zeolite treated with H_2O_2 , c) K-exchanged zeolite, d) Ca-exchanged zeolite

Table 2 reports the total weight loss for all cation forms determined by TG analysis. The zeolite water loss is higher in the zeolites exchanged with bivalent ion. Thermal analysis results (Table 2) point out the loss of more weight for modified zeolite (Fungaro et al., 2010). In addition, in the monovalent ions, the larger cations have less zeolite water (Table 3). When zeolite samples with and without adsorbed MB were compared, MB adsorbed zeolite samples showed greater weight loss (Fig 6).

Table 2. The results of thermal analysis of natural and modified natural zeolite samples

Sample	Weight Loss (%)
Natural zeolite	12.084
Zeolite treated with H ₂ O ₂	13.734
K- exchanged zeolite	12.974
Ca-exchanged zeolite	14.149

The presence of different exchangeable cations in zeolites changes their temperature at which water is lost from them. TGA curves of natural and modified zeolites are shown in Figure 6. In the temperature range 25–100 °C, the weight loss is due to desorption of physisorbed water. The results vary depending on the type of zeolite and the treatment conditions as Ca-Exchanged > K-Exchanged > Natural Zeolite. After K- and Ca-exchange and H₂O₂ treatment, the amount of water adsorbed decreases, which is a result of the lack of extra framework cations and dealumination.

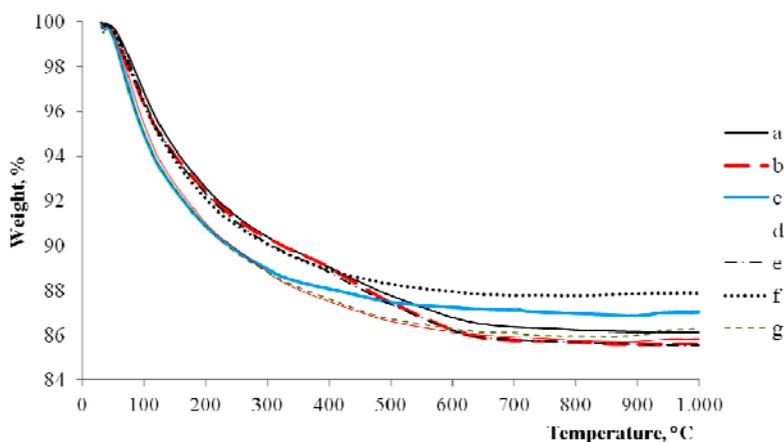


Figure 6. Thermal analysis of zeolite samples: a) MB adsorbed natural zeolite, b) MB adsorbed zeolite treated with H₂O₂, c) K-exchanged zeolite, d) Ca-exchanged zeolite, e) MB adsorbed Ca-exchanged zeolite, f) natural zeolite, and g) zeolite treated with H₂O₂

In Ca- and K-exchanged zeolites, the major portions of water molecules are weakly associated with zeolites because of the restriction of water molecules in the defects formed by dealumination. Based on the results mentioned before, the water molecules in zeolites can be classified into three forms as physisorbed water (<100 °C), water associated with extra-framework cations and aluminium (100–400 °C), and water associated with silanol nests (>400 °C). The water exist in clinoptilolite – rich zeolites is more stable up to 700 °C. However, stability decreases in the zeolites containing mordenite and clinoptilolite. Because of the decrease in the amount of cations after H₂O₂ treatment, the water content in Ca-exchanged zeolite is significantly decreased.

Sorption on natural and modified zeolite

Natural zeolite, zeolite activated with H_2O_2 , K-exchanged zeolite activated with H_2O_2 , and Ca-exchanged zeolite activated with H_2O_2 were applied to MB solutions. Contact time, initial MB concentration, pH, adsorbent dosage, temperature and agitation speed were the parameters to find out the optimum conditions for the adsorption. To determine equilibrium time in adsorption process, while other variables are kept constant only concentration change depending on stirring time was analyzed. Solutions of 50 mg dm^{-3} concentration of MB prepared from a stock solution at $\text{pH} = 7$ and 300 rpm were mixed with 0.05g zeolite.

As shown in Fig 7a, the adsorption has reached the equilibrium in 30 minutes. q_t is the ratio of adsorbed amount of MB to per gram of zeolite. MB adsorption on zeolite increases with an increase in adsorption time, and come to equilibrium at 30min. At 50 mg dm^{-3} dye concentration and $\text{pH} 7.0$, when the contact time reached from 30min to 240min, the adsorbed amount of MB raised 19.1 mg/g to 21.1 mg/g for natural zeolite, 31.0 mg/g to 32.0 mg/g for K- exchanged zeolite, and 34.0 mg/g to 36.0 mg/g for Ca- exchanged zeolite. The shortest contact time for adsorption was shown as 10 minute in a study by Özdemir (2008) among other studies. However, while Özdemir refers adsorbed amount of MB as 1.25 mg/g, in this study, adsorption comes to equilibrium in 30 minutes with 36 mg/g sorption

Another factor affecting particles adsorbed on dyes is acidity of solution (pH). It is generally expected that adsorption will increase with increasing pH. It is advantage for cationic MB that zeolite surface has negative charge pHs above 6. In Fig.7b, there is no significant change recorded in the amount of MB adsorption at pH between 1 and 8. Increase in adsorption at pHs between 9 and 12 is relatively less than increase in adsorption at pHs between 13 and 14 because of precipitation of MB over pH 8. Therefore, it is decided that there was no contribution made to adsorption amounts by pH over 8, and experiments were set to pH 7. The values for adsorbed amount of MB by zeolite, K-exchanged zeolite and Ca- exchanged zeolite were shifted 20.1 mg/g to 22.4 mg/g, 29.0 mg/g to 35.0 mg/g, and 30.5 mg/g to 38.0 mg/g, respectively when pH increased 3 to 8. Because of the electrostatic attraction force that with increasing pH adsorbed MB onto zeolite surface was increased. It is natural that surface charge of zeolite in alkaline media is negative and cationic MB molecules are kept more on the surface of zeolite at high pH values (Jin et al., 2008). Fungaroa et al. (2010) point out pH for zeolite as 5, but this study shows that best pH value is found 7 because zeta potential value of zeolite is negative over 6 which attracts cationic dyes like MB.

Varying the starting concentration of MB (not shown in Figures) between 50 and 600 mg/dm^3 showed a slight increase in the amount of MB adsorbed. While at 50 mg/dm^3 of C_0 adsorption percentages are 50% for zeolite, 74% for K-exchanged zeolite and 76% for Ca-exchanged zeolite, over 100 mgL^{-1} adsorption percentages dropped clearly as 20% for zeolite, 33% for K-exchanged zeolite and 36% for Ca-exchanged zeolite. This showed that adsorption capacity of zeolite samples for over 100 mg dm^{-3}

initial MB concentration was exceeded, and after 100 mg/dm³ even modification of zeolite did not affect the adsorption capacity.

For adsorbent dosage, increasing amount of natural and modified zeolite had caused an increase in the amount of adsorbed MB concentration between 0.01g and 0.5g (see Fig.7c). MB adsorption is slightly increased over 0,05g adsorbent added into the mixture. Ozdemir (2012) states that 100 mg/L for initial concentration of MB is optimum same as in this study, while that study finds out adsorbed amount 46.31 mg/g, the adsorbent dosage is used as 0.1 g which is 0.05 g zeolite in this study.

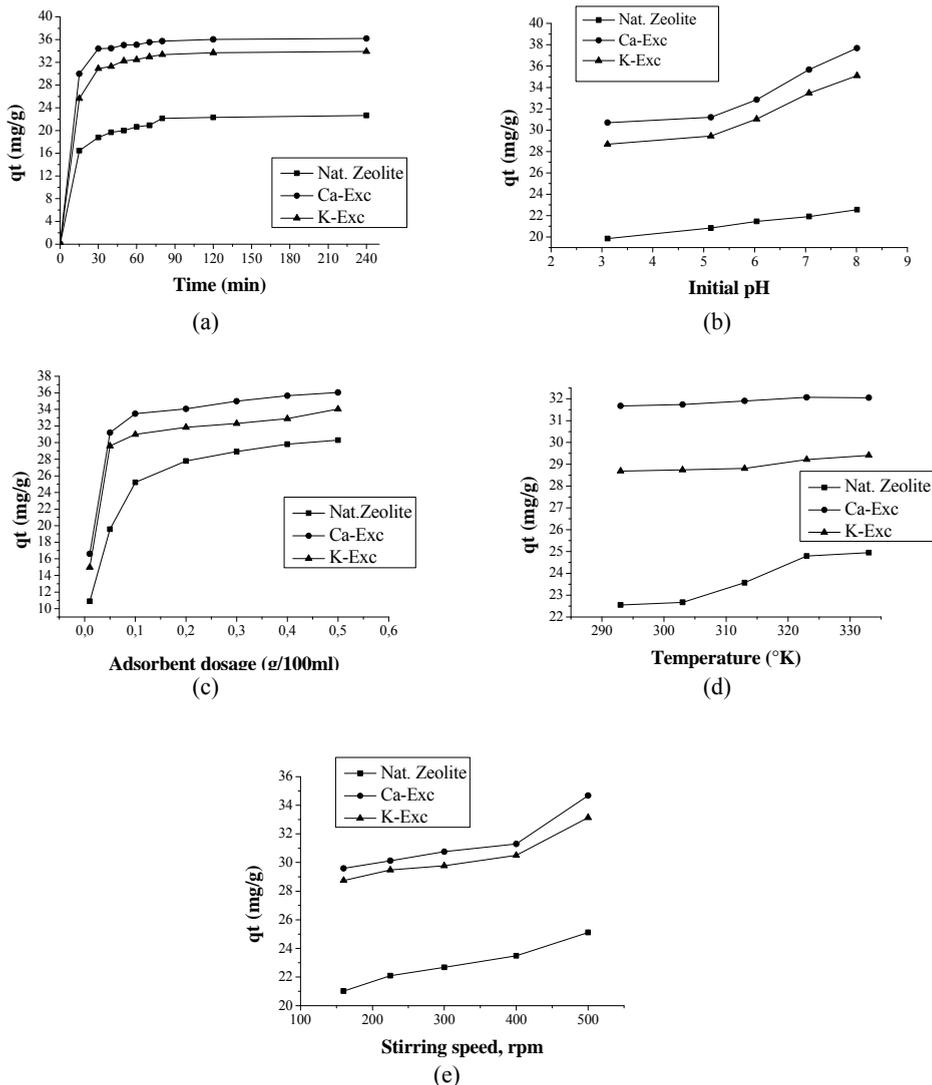


Figure 7. Effects of (a) time, (b) pH, (c) adsorbent dosage, (d) temperature, and (e) stirring speed on MB adsorption by natural zeolite, K-exchanged zeolite, and Ca-exchanged zeolite

Besides the variables considered above, there are also two more variables as temperature and mixture rate used in adsorption. As seen in Fig. 7d, because there is a slight increase in adsorption from 22.0 mg/g toward 26.0 mg/g for natural zeolite, and 29.0 mg/g to 30.0 mg/g for K-exchanged zeolite, 31.0 mg/g to 32.0 mg/g for Ca-exchanged zeolite with increase in temperature from 20 °C to 60 °C. With increase in temperature, MB molecules try harder to get in zeolite pores. Attraction between hydroxyl groups holding on zeolite surface and cationic methylene groups can cause this kind of raise (Bissada et al., 1967). However, in physical adsorption change in temperature does not have influence on increase in adsorption.

In Fig. 7e, it is clear that there is no significant difference in contribution of adsorption percentage with stirring speed at 150, 225, 400 and 500 rpm, respectively. Therefore, the mixture rate is determined as 150rpm. The trend of change with stirring speed pointed out that contacting MB ions with zeolite samples by increasing speed did not cause the raise for adsorption capacity

Table 3. Previous studies on MB adsorption and the maximum amounts adsorbed

Type of adsorbent	Initials conditions	Adsorbed amount of MB (mg/g)	Ref.
Clay	0.1 g; 100 cm ³ ; 100 mg/dm ³ ; 60 min	60	Gürses et al. (2006)
Perlite	1 g; 100 cm ³ ; 93.475 mg/dm ³ ; 30 min; pH = 7	7.5	Doğan et al. (2004)
Natural zeolite	2.2434 mg/dm ³ ; 150 cm ³ ; 1000 min; 0.01–0.05g	23.6	Farhade and Aziz (2010)
Hazelnut shell	50 cm ³ ; 0.25 g; 24 h; 959.58 mg/dm ³	96.0	Doğan et al. (2008)
Hazelnut shell	1 g; 2 dm ³ ; 40 min; 37.39 mg/dm ³ ; pH = 4.1–4.5	74.8	Doğan (2009)
Zeolite	12.8 mg/dm ³ ; 100 cm ³ ; 1 g; 10 min; pH = 5	1.3	Fungaroa et al. (2010)
Melamine-urea resin	13.04 mg/dm ³ ; 0.3 g; 20 min; 1 dm ³	12.1	Özdemir (2008)
Sepiolite	400.32 mg/dm ³ ; 2 dm ³ ; 5 g; 400 rpm; pH = 5–9; 3 h	75.1	Doğan et al. (2007)
(SDBS)- and (SDS)-modified zeolite	25 mg/dm ³ ; 25 cm ³ ; pH = 6.43; 0.1 g; 30 min	8.7	Jin et al. (2008)
Tripoli	100 cm ³ ; 0.5 g; 100 mg/dm ³ ; pH = 8	17	Alzaydien (2009)
Activated carbon	0.1 g; 50 cm ³ ; 1–60 min; 100 mg/dm ³	46.3	Ozdemir (2012)
Vineyard pruning waste	25 °C and natural pH; 10 g/2 dm ³ ; 400 rpm; 60 min	46.1	Ugurlu (2010)
Natural zeolite	0.05 g; 100 cm ³ ; 30 min, 100 mg/dm ³	28.6	present study
Modified zeolite	0.05 g; 100 cm ³ ; 30 min, 100 mg/dm ³	42.7	

The optimum pH range for adsorption of MB was found to be at 7.0. Adsorption equilibrium attained within 30 minutes. The sorption of MB slightly increased with

rise of temperature. As the zeolite amounts increased, the removal efficiencies increased, but on the other hand, the adsorbed amount on the zeolite decreased with the increasing zeolite amounts. The removal efficiency of natural zeolites is strongly affected by the modification of zeolite. Overall, a comparison of several adsorbents employed for MB adsorption in previous research efforts was presented in Table 3. As it can be seen from Table 3, modified zeolite employed in this work presented higher adsorption capacity when compared with some of adsorbent reported in the literature.

Adsorption equilibrium

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent, and is important in the design of adsorption system. As shown in Table 4, the adsorption increases with the increasing equilibrium concentration and approaches to equilibrium at higher concentration. Higher temperature slightly results in higher adsorption capacity.

Two models are commonly used to simulate the adsorption isotherm, the Langmuir and Freundlich isotherms. The well-known expression of the Langmuir model is

$$q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the equilibrium dye concentration on adsorbent (mg/g), C_e the equilibrium dye concentration in solution (mg/L), q_{\max} is the monolayer capacity of the adsorbent (mol/g) and K_L is the Langmuir adsorption constant (dm^3/mg) which relates to the adsorption energy. The Langmuir equation is applicable to homogeneous sorption, where the sorption of each sorbate molecule onto the surface has equal sorption activation energy. On the other hand, the Freundlich equation is

$$q_e = K_F C_e^{1/n} \quad (2)$$

where q_e is the equilibrium dye concentration on adsorbent (mg/g), C_e is the equilibrium dye concentration in solution (mg/L) and K_F (L/g) and n are the Freundlich constants characteristic of the system, indicators of adsorption capacity and adsorption intensity, respectively. The Freundlich equation is employed to describe heterogeneous systems and reversible adsorption and is not restricted to the formation of monolayers.

The adsorption of MB on zeolite is due to the formation of the hydrogen bonds between surface hydroxyls and dye molecules with participation of water molecules. The non-linear forms of the two isotherms to the experimental data are illustrated in Table 4. The fits for two isotherms are quite similar. Except for K-exchanged zeolite at 50 °C which shows both Langmuir and Freundlich type of isotherm, all other experimental data were well fitted to the Langmuir equation, with good correlation coefficients (Alzaydien, 2009). The correlation coefficients of Ca-exchanged zeolite at both 20 °C and 50 °C and K-exchanged zeolite at 50 °C for two models are greater

than 0.95, indicating that the two models fit the experimental well. For other samples, Langmuir is the only isotherm fits for MB adsorption. For all zeolite samples, Langmuir isotherm correlations belong to 20 °C are higher than the values of 50 °C. This would lead us that temperature does not influence on adsorption. For K_L values, all values decreased with increasing temperature, the highest value was shown for Ca-exchanged zeolite.

The Langmuir model suggests the surface sorption mechanism. The maximum Langmuir equilibrium constant (K_L) calculated from the slope and the intercept of the linear plot were 26.11 mg g⁻¹ at 20°C and it belongs to Ca-exchanged zeolite. The value of the monolayer saturation capacity of zeolite was comparable to the adsorption capacities of some other adsorbent materials for MB (Table 4). A direct comparison of literature data obtained using different adsorbents may not be appropriate since experimental conditions are not systematically the same.

Freundlich constant (K_F) and the heterogeneity factor ($1/n$) calculated from the slope and the intercept of the linear plot were changing between 45.42 mg g⁻¹ and 722.00 mg g⁻¹, 0.26 and 3.14, respectively. The value of $1/n$ smaller than 1 points out the favorable sorption conditions (Alzaydien, 2009; Chavez et al., 2010). In this manner, Ca-exchanged and K-exchanged zeolite samples were favorable. The Langmuir and Freundlich isotherm constants and linear (R^2) regression coefficients are shown in Table 4.

Table 4. Langmuir and Freundlich isotherms of MB adsorption on natural zeolite, Ca-exchanged and K-exchanged zeolite

	Langmuir Isotherm			Freundlich Isotherm		
	K_L , mg/g	b , L/mg	R^2	$1/n$	K_f , mg/g	R^2
Zeolite (20 °C)	2.845	0.016	0.971	1.891	89.125	0.916
Zeolite (50 °C)	0.053	0.007	0.959	1.748	98.628	0.893
Ca-Exc (20 °C)	26.110	0.568	0.998	0.260	45.420	0.961
Ca-Exc (50 °C)	0.142	0.132	0.996	2.741	221.310	0.973
K-Exc (20 °C)	20.534	0.003	0.988	0.437	87.510	0.804
K-Exc. (50 °C)	0.149	105.68	0.987	3.140	722.000	0.988

Conclusions

The effectiveness of H₂O₂ in activating the natural and modified zeolites to remove methylene blue (MB) ions from aqueous solutions has been presented. It was observed that MB adsorption is partially dependent on the adsorbent amount, particle size, contact time, initial pH of the solution and initial metal concentration.

FTIR, SEM, TG/DTA analyses revealed that Ca- and K-exchanged zeolites have higher surface area and affinity toward MB. Modification after H₂O₂ treatment allowed zeolite samples to adsorb more MB ions than untreated zeolite samples. The effect of activation with H₂O₂, and then modification with KCl and CaCl₂ could

significantly improve the adsorption rate and adsorption capacity of MB ions. Adsorption values were arisen with activation and modification as Ca-Exchanged Zeolite (H_2O_2 treatment) > K-Exchanged zeolite (H_2O_2 treatment) > Zeolite treated with peroxide > natural zeolite.

The adsorption of MB on zeolite was found to conform to the Langmuir equation. This study has shown the potential of modified zeolites after H_2O_2 treatment for the removal of MB from wastewater streams due to their relatively low price, abundance in nature, and its easy procedure to modify.

References

- ALBAYRAK M., 2008, *Batu Anadolu, Trakya, Kapadokya Yöresi Zeolitleri Mineralojik Veri Kitabı*, MTA Rap., 11053. (in Turkish)
- ALKAN M., DEMIRBAS O., DOĞAN M., 2007, *Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite*, Microporous and Mesoporous Materials, 101, 388–396.
- ALZAYDIEN A.S., 2009, *Adsorption of Methylene Blue from Aqueous Solution onto a Low-Cost Natural Jordanian Tripoli*. American Journal of Environmental Sciences. 5(3), 197–208.
- ARMAGAN B., OZDEMIR O., TURAN M., CELIK M.S., 2003, *The removal of reactive azo dyes by natural and modified zeolites*, Journal of Chemical Technology and Biotechnology. 78, 725–732.
- ATEŞ A., HARDACRE C., 2012, *The effect of various treatment conditions on natural zeolites: Ion exchange, acidic, thermal and steam treatments*. Journal of Colloid and Interface Science, 372, 130–140.
- ATES A., REITZMANN A., HARDACRE C., YALCIN, H., 2011, *Abatement of nitrous oxide over natural and iron modified natural zeolites*, Applied Catalysis A: General, 407(1–2), 67–75.
- AJEMBA R.O., ONUKWULI O.D., 2013, *Adsorptive removal of colour pigment from palm oil using acid activated Nteje clay. Kinetics, equilibrium and thermodynamics*, Physicochemical Problems of Mineral Processing, 49(1), 369–381.
- BISSADA K.K., JOHNS W.D., CHENG F.S., 1967, *Cation-Dipole interactions in Clay Organic Complexes*. Clay Minerals, 7, 155–166.
- CAGLAR B., AFSIN B., TABAK A., EREN, E., 2009, *Characterization of the cation-exchanged bentonites by XRPD. ATR, DTA/TG analyses and BET measurement*. Chemical Engineering Journal, 149, 242–248.
- CHAVEZ M.L., DE PABLO L., GARCIA T.A., 2010, *Adsorption of Ba^{2+} by Ca-exchange clinoptilolite tuff and montmorillonite clay*. Journal of Hazardous Materials, 175, 216–223.
- CRINI G., 2006, *Non-conventional low-cost adsorbents for dye removal: A review*. Bioresource Technology, 97, 1061–1085.
- DEMIRHAN M., 1998, *Manisa İli-Demirci İlçesi Akdere Köyü ONIR-6645 Ruhsat No'lu Zeolit Sahası Maden Jeolojisi Raporu*, MTA Rap., 10173. (in Turkish)
- DOĞAN M., ABAK H., ALKAN M., 2008, *Biosorption of Methylene Blue from Aqueous Solutions by Hazelnut Shells: Equilibrium, Parameters and Isotherms*. Water Air Soil Pollution, 192, 141–153.
- DOĞAN M., ABAK H., ALKAN M., 2009, *Adsorption of methylene blue onto hazelnut shell: Kinetics, mechanism and activation parameters*. Journal of Hazardous Materials. 164, 172–181.
- DOĞAN M., ALKAN M., OZDEMIR Y., 2000, *Adsorption of Methylene Blue from aqueous solution onto perlite*. Water, Air & Soil Pollution, 120 (3–4), 229–248.
- DOĞAN M., OZDEMIR Y., ALKAN M., 2007, *Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite*. Dyes and Pigments, 75(3), 701–713.

- ETAIW S.E.H., EL-BENDARY M.M., 2012, *Degradation of methylene blue by catalytic and photocatalytic processes catalyzed by the organotin-polymer $^3_{\infty}[(Me_3Sn)_4Fe(CN)_6]$* , Applied Catalysis B: Environmental, 126, 326–333.
- FARHADE J., AZIZ H., 2010, *Competitive Adsorption of Methylene Blue and Rhodamine B on Natural Zeolite: Thermodynamic and Kinetic Studies*. Chinese Journal of Chemistry. 28, 349–356.
- FUNGAROA D.A., GROSCHEA L.C., PINHEIROB A.S. IZIDOROA J.C., BORRELY S.I., 2010, *Adsorption of methylene blue from aqueous solution on zeolitic material and the improvement as toxicity removal to living organisms*. Orbital Electronic Journal of Chemistry. 2(3), 235–247.
- GLADYSZ-PLASKA A., KOWALSKA-TERNES M., MAJDAN M., 2000, *Adsorption of toxic metal ions on zeolites*. Przem Chem. 79:298.
- GULGONUL I., 2012, *Evaluation of Turkish Bentonite for Removal of Dyes from Textile Wastewaters*, Physicochemical Problems of Mineral Processing, 48(2), 369–380.
- GÜMÜŞ D., AKBAL F., 2011, *Photocatalytic Degradation of Textile Dye and Wastewater*, Water, Air & Soil Pollution, 216, 21–37.
- GÜRSES A., DOĞAR C., YALÇIN M., AÇIKYILDIZ M., BAYRAK R., KARACA S., 2006, *The adsorption kinetics of the cationic dye, methylene blue, onto clay*. Journal of Hazardous Materials, 131, 217–228.
- HAN R., ZOU L., ZHAO X., XU Y., XU F., LI Y., WANG Y., 2009, *Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column*, Chemical Engineering Journal, 149, 123–131.
- HERNANDEZ M.A., CORONA L., ROJAS F., 2000, *Adsorption characteristics of natural erionite, clinoptilolite and mordenite zeolites from Mexico*. Adsorption, 6, 33–45.
- HERNANDEZ-RAMIREZ O., HOLMEZ S.C., 2008, *Novel and modified materials for wastewater treatment applications*. Journal of Materials Chemistry, 18, 2751–2761.
- JIA A., LOU L., ZHANG C., ZHANG Y., LIU S., 2009, *Selective oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide over alkali-treated ZSM-5 zeolite catalysts*. Journal of Molecular Catalysis A: Chemical, 306, 123–129.
- JIN X., JIANG M., SHAN X., PEI Z., CHEN Z., 2008, *Adsorption of methylene blue and orange II onto unmodified and surfactant-modified zeolite*. Journal of Colloid and Interface Science. 328, 243–247.
- KARAOĞLU M.H., UGURLU M., 2010, *Kinetic and equilibrium studies of methylene blue biosorption by vineyard pruning waste*. Fresenius Environmental Bulletin, 19(12b), 3199–3208.
- KONDRU A.K., KUMAR P., CHAND S., 2009, *Catalytic wet peroxide oxidation of azo dye (Congo red) using modified Y zeolite as catalyst*. Journal of Hazardous Materials, 166, 342–347.
- KORKUNA O., LEBODA R., SKUBISZEWSKA-ZIĘBA, J., VRUBLEVS'KA T., GUŃKO V.M., RYCZKOWSKI J., 2006, *Structural and physicochemical properties of natural zeolites: Clinoptilolite and mordenite*. Microporous Mesoporous Materials, 87, 243–254.
- KOWALCZYK P., SPRYNSKY M., TERZYK A.P., LEBEDYNETS M., NAMIESNIK J., BUSZEWSKI B., 2006, *Porous structure of natural and modified clinoptilolites*, Journal of Colloid and Interface Science, 297, 77–85.
- MISAELEIDES P., 2011, *Application of natural zeolites in environmental remediation: A short review*, Microporous and Mesoporous Materials, 144, 15–18.
- METES A., KOVACEVIC D., VUJEVIC D., PAPIC S., 2004, *The role of zeolites in wastewater treatment of printing inks*, Water Research, 38, 3373–3381.
- OZDEMİR C.S., 2012, *Adsorption and desorption kinetics behavior of methylene blue onto activated carbon*. Physicochemical Problems of Mineral Processing, 48(2), 441–454.

- OZDEMIR F.A., 2008, *Atıksulardan boya giderimi için yeni bir yöntem*. Unpublished Master thesis. Istanbul Technical University Institute of Sciences.
- SLOKAR Y.M., MARECHAL A.M.L., 1998, *Methods of decoloration of textile wastewaters*. Dyes and Pigments, 37(4), 335-356.
- WANG S., PENG Y., 2010, *Natural zeolites as effective adsorbents in water and wastewater treatment*. Chemical Engineering Journal, 156,11-4.